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INVESTIGATION OF ISOTOPIC EXCHANGE OF IODINE BETWEEN SODIUM IODIDE AND ETHYL IODIDE IN AN ALCOHOL SOLUTION

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The method for concentrating radioactive isotopes suggested in 1934 by Szillard and Chalmers (1) in the case of concentrating I^{128} presupposes the absence of an exchange reaction between C_2H_5I and I'. The question of the exchange between ethyl iodide and NaI in various solvents has been qualitatively studied by a number of researchers (2-5), who showed that the exchange proceeds slowly in alcohol solutions at low temperatures, and more rapidly at 100 degrees centigrade.

In 1942-43 two investigations (6, 7) were published in which the exchange between ethyl iodide and NaI in alcohol solutions was studied quantitatively. The 25-minute isotope of iodine I^{128} was used in these investigations, and for that reason the duration of the kinetic experiments was limited to several hours.

In this study, a mixture of long-lived radioactive isotopes of iodine was used, a fact which permitted more lengthy experiments to be conducted and also made it possible to expand the investigation into the field of low temperatures. The technique of the preparation and extraction of radioactive isotopes of iodine has been described in previous articles (8, 9) by Neyman and other collaborators.

Active sodium iodide was prepared according to the reaction:

$$Na_2S + I_2 = 2NaI + S.$$

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The liberated sulfur was filtered off, and the NaI containing inactive NaI was dissolved to form a 0.2 N solution in alcohol. Before initiating the kinetic experiment, this solution was mixed with an equal volume of a 0.2 N alcohol solution of ethyl iodide. The solutions were first heated or cooled to the temperature of the experiment.

Therefore, the experiment was conducted with solutions in which $[NaI] = [C_2H_5I] = 0.1$ mol per liter. The small flasks containing the solutions were placed in a thermostat and the temperature was kept constant.

While the reaction was in progress, samples were taken and rapidly cooled, after which separation of the mixture was accomplished by shaking it up with benzene. Then, after separation of the water layer containing dissolved I ions, precipitation with $AgNO_3$ was carried out. The ethyl iodide of the benzene layer was subjected to hydrolysis, after which the radioiodine was transferred into AgI. A Geiger-Mueller counter was used to investigate the AgI precipitate.

In all of the experiments, a part of the NaI to be mixed with ethyl iodide was precipitated with $AgNO_3$, and the active precipitate of AgI used as a control.

Results of the experiments performed in connection with this study at temperatures of 10, 20, 30, 40, and 80 degrees centigrade are given in the following table:

Kinetics of Exchange of Iodine between NaI and C_2H_5I at Different Temperatures ($[NaI] = [C_2H_5I] = 0.1$ mol per liter)

Temp in °C	Temp in hr	Activity C_2H_5I	Activity NaI	Activity ΣI	Activity Indicator	$k.10^4$ liter mol/second
10	5	17	265	282	282	
	10	19	244	263	270	0.23
	15	20	227	247	249	
	24	21	201	222	231	
20	10	48	153	201	208	
	17	59	120	179	180	0.92
	24	53	87	140	136	
30	2	49	177	226	228	
	4	54	163	217	219	
	6	64	149	213	213	
	8	69	139	208	209	
	10	71	133	204	206	2.15
	16	50	60	110	112	
	20	49	55	104	104	
	24	46	48	94	97	
40	3	78	155	223	243	
	5	75	123	198	200	4.2
	10	71	81	152	148	
	12	65	68	133	142	
80	5 min.	50	138	188	180	
	10 "	78	104	182	182	153
	20 "	90	94	184	182	

If the reaction of isotopic exchange investigated in this instance is bimolecular, its rate constant can be expressed by the following formula:

$$k = \frac{1}{(a+b)t} \ln \frac{1}{1-(1+\frac{b}{a})\frac{x}{c}} \qquad (1)$$

In the present case, where $a = [C_2H_5I] = b = [NaI] = 0.1$, formula (1) is reduced to the form:

$$k = \frac{11.5}{t} \lg \frac{1}{1-2\frac{x}{c}} \qquad (2)$$

where c is the total activity of the iodine (equal to the activity of the control) and x is the activity of the ethyl iodide.

Results of the experiments of this study are depicted on a graph the coordinates of which are $\frac{1}{1-2\frac{x}{c}}$ and t.

As concerns the measurement of the magnitude x/c of isotopic exchange of C_2H_5I and NaI with time, the experimental points after being plotted lie on straight lines originating from the 0 point of the graph, which fact verifies the applicability of formula (2) to the reaction investigated. Values for the constants of the rate of isotopic exchange, derived from the slopes of the lines plotted are given in the last column of the above table.

To determine the energy of activation of the exchange reaction investigated here, the values for the constants were plotted in a graph with the coordinates lg k and 1,000/T. The points lie on a straight line along the slope of which may be found the value E = 19,000 cal/mol. This quantity, within the limits of error for the experiments, corresponds with the values for energy of activation found in the works (6, 7).

If, based on the equation for the constant of the rate of the bimolecular reaction

$$k = P\frac{No}{1000} \sigma^2 \sqrt{\frac{8\pi RTM_1M_2}{M_1 \quad M_2}} e^{-E/RT} \qquad (3)$$

it is assumed that the value for the steric factor P = 0.1, and the values for k and E determined by Neyman and Protsenko are substituted, then a plausible value for the effective diameter $\sigma \cong 3.10^{-8}$ cm is obtained.

[The graphs described above are available in the original document in CIA.]

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